Characterization of Graphene Flakes Produced with Ultrasonication in N-Methyl-Pyrrolidone (NMP)

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A R T I C L E   I N F O

A B S T R A C T

In this study, graphene flakes (GFs) were prepared from ultrasonication of graphite nanoplatelets (GNPs) in N-methylpyrrolidone (NMP) as solvent. The study was undertaken to evaluate the effect on GFs' sizes and thicknesses by different powers (310W – 180W) and the time (3 minutes – 300 minutes) of ultrasonication. From this study, clearly that the two variables affected the condition of GFs. Transmission electron microscopy (TEM) shows that the size of the GFs is at the optimum size when using 180W of ultrasonication power for 3 minutes (~2.3μm) with high thickness whereas the minimum size is about 0.6μm after using 310W of ultrasonication power for 300 minutes. The ratio of D band intensity to the 2D band intensity (I_D/I_{2D}) of Raman Spectroscopy shows that, as the time and power of ultrasonication increases, the thickness of GFs is reducing. Raman spectroscopy and thermal gravimetric analysis (TGA) were used to investigate the graphitic characteristics and thermal stability of the exfoliated GNPs. GFs produced are stable up to 1000°C. The ultrasonication method in NMP can be used to produce GFs and facilitates to a broad range application of graphene such as in polymer composites and lithium ion batteries.

INTRODUCTION

Graphene is the two dimensional (2D) building block for carbon allotropes of every other dimensionality. It can be stacked into 3D graphite, rolled into 1D nanotubes or wrapped into 0D fullerenes (Ferrari, 2007). It is a very important carbon material that has attracted considerable attention owing to its high aspect ratio, small radius of curvature, high mechanical strength, unique electrical properties and chemical stability than other other reinforced materials such as CNTs, fibers of carbon and Kevlar (Singh *et al*.,2011). By exfoliation of graphite in liquid phase, graphene sheets can be obtained in large scale under sonication process (Wei and Liu, 2010). It has been studied for sixty years but only 40 years later it has been realized that graphene provides excellent properties to be used in applications such as polymer composites, semiconductor and lithium batteries. Because of its unique properties, its reinforcing properties can offer different and exceptional properties in aerospace, electronics and automotive field. Many researchers have been synthesized graphene using different techniques.

The first technique has been introduced by Novoselov and Geim using mechanical exfoliation or scotch tape method by repeated peeling (Terrones *et al*., 2011). Mechanical exfoliation provides the simplest way to prepare single- or few-layer graphene but in a small amount of samples (Young *et al*., 2012). Mechanically exfoliated and epitaxially grown graphene films exhibit high quality but are not suitable for large-scale production (Su *et al*., 2011), while chemical oxidation of graphite into graphite oxide offered an easy path to obtain graphene oxide in large quantity that can be reduced chemically, electrochemically or thermally into graphene. Chemical vapour deposition (CVD) methods have shown to be another suitable technique for achieving a large scale production of graphene, but the process requires high temperature (~1,000 °C) for operating and costs a lot of money (Puangbupphaa *et al*., 2012). The rise of interest towards graphene and the needs of high volume of graphene for applications such as composites lead to the investigation of large scale exfoliation (Young *et al*., 2012). Thus, the exfoliation of graphite in liquid phase gives a promising route to produce graphene-like materials (Hernandez *et al*., 2009). N-methylpyrrolidone (NMP) was chosen in this research because the surface tension close to 40mJm^{-2} and suitable for direct exfoliation of graphene (Zhang *et al*., 2010). In this report, we demonstrate that graphene can be exfoliated from GNPs using NMP as the solvent and ultrasonic treatment with various types of ultrasonication power. It is an easy method with a simple

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preparation and low cost. The GNPs were ultrasonicated in NMP with different times (3-300 minutes). GFs were extracted as the sediment after ultrasonication in NMP solution. TEM and Raman spectroscopy measurement were used to investigate the size and thickness of GFs.

MATERIALS AND METHODS

Graphite nanoparticles (GNPs) were produced by XG Science USA (5.4µm nominal average size and 5-10nm (15-30 layers) thick), whereas NMP was purchased from Nacalai Tesque. GNPs (50mg) were added into a sonicating glass tube that contained 50ml of NMP. The dispersion was ultrasonicated using the bath ultrasonic processor (Yamato) at temperature 11°C ± 1°C running in four different powers (310W , 250W, 280W and 150W) and time ranging from 3 minutes to 300 minutes for each power. NMP has high boiling point properties. Therefore the water bath temperature was set low to prevent temperature increased and degradation of the NMP solution during sonication . After sonication, the dispersions transferred to polymer vials for centrifugation (CN-2060 manufactured by AS ONE) process to separate the graphene sediments from the solvent. Each vial contained 15ml of graphene dispersion in NMP and 15ml of EtOH. Centrifugation was performed at 5000 rpm for 60 minutes. After the centrifugation process, graphene sediments were attached to the wall of the vials leaving the supernatant liquid. The resulting sediments were eluted with some ethanol to remove the trace material from the decomposed NMP. This solution was then dried at 100°C for about 1 hour to evaporate the ethanol and left behind GFs for the further evaluation process.

The morphology of sediments was investigated using transmission electron microscope (TEM, Hitachi H-800) operating at 100kV. The quality of exfoliated GFs was determined by using Raman spectroscopy and thermogravimetric analysis; TGA (SII EXSTAR 6000). The Raman spectroscopy (Horiba XploRa) had an excitation wavelength of 488nm. TGA was performed by heating samples at least more than 5mg for each condition from 30°C to 1000°C at a heating rate of 10ºC/min under nitrogen atmosphere (constant 300ml/min N_2 flow) using alumina as the sample pan.

RESULTS AND DISCUSSION

Transmission electron microscopy (TEM) observations:
GNPs and GFs had been observed using TEM in each of the ultrasonication's conditions. Fig. 1 shows that as the time and output power of ultrasonication increase, the thickness and size of the GFs were reduced. The average size of GNPs was 5.4 µm. From the Fig. 1a, it can be seen that the image of the GNPs was darker indicated that the GNPs was thicker compared to the other three images (Fig. 1b-1d). No of layers of GNPs seemed to be difficult to identify because many layers are stacked to one another. The images of GFs (Fig. 1b-1d) were brighter proving that the layers of GNPs became thinner after being sonicated. The average size of GFs in Fig. 1b and Fig.1d were 2.2µm and 0.6µm respectively.
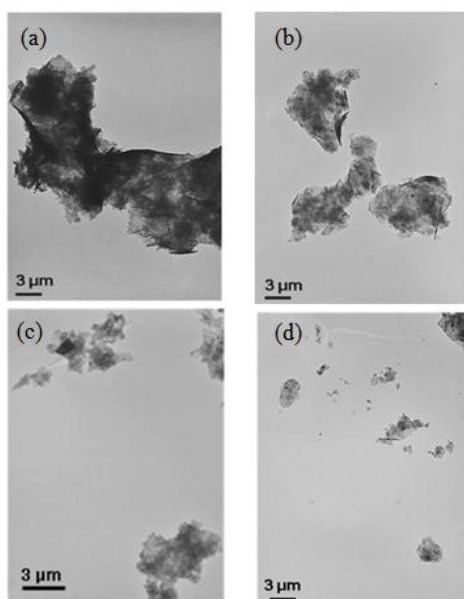

Fig. 1: (a) TEM image of raw material, GNPs (b) GFs (180W, 3min).

The longer sonication time may encourage better result on the exfoliation of graphene, but at the same time it may decrease the planar size of the graphene (Puangbupphaa *et al.*, 2012). From this figure, it can be concluded that the size of GFs was decreased by increasing the sonication time and output power.

Fig.2 is a graph plotting the average size of the GFs of sonication for each condition. The sizes were rapidly changed from 5.4µm to about 2.2µm between 0 min to 3 mins for all powers except for 310W and then gradually decreased at the remaining time (until 300 minutes).
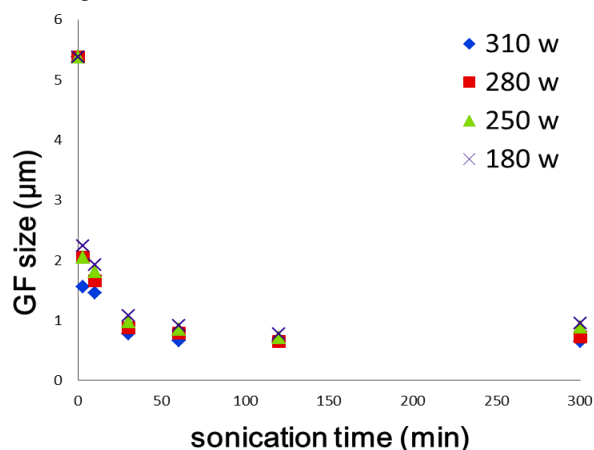

Fig. 2: The average size of each ultrasonication irradiation conditions.

Raman Spectroscopy Analysis:

Raman spectroscopy is a fast and non-destructive analysis tool which provides high-throughput and unambiguous identification of the properties of graphene films with three most intense peaks: Disorder-related D peak at ~1350 cm^{-1}, the G peaks at ~1590 cm^{-1} and 2D (or G') peak at ~2700 cm^{-1}, respectively. The D band usually provides the information on defects in the crystalline structure of graphene layers, G band is for in plane vibration of sp^2 carbon atom while the 2D band for stacking order (number of layers) (Ni *et al.*, 2008). For more than 5 layers, the Raman spectrum is hardly distinguishable from the bulk graphite (Ferrari *et al.*,2011). Based on the Fig.3, the 2D bands were hardly distinguishable from GNP and graphite except that graphite has lower intensity from the rest GFs and GNPs, even though exfoliation was enhanced according to microstructural observation such as TEM. It can be concluded that each condition of GFs contained more than 5 layers.
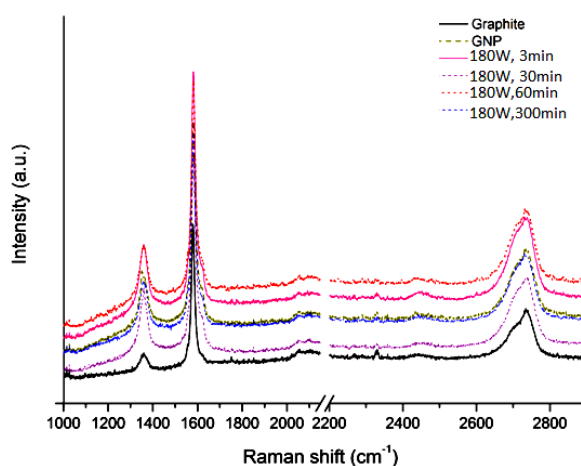

Fig. 3: Raman spectra of GNPs, graphite and GFs with sonication power of 180W.

However that doesn't mean that the thickness of GFs produced does not make any difference from the starting material, GNPs, but it cannot be identified with Raman spectroscopy because of more than 5 layers. Based on the TEM images the exfoliation of GFs produced was increased with increasing of power and time of ultrasonication. Although current research focus mainly on single and bilayer graphene, but multi-layers graphene also exhibit two dimensional properties that contributed to interesting properties (Ni *et al.*,2008).The ratio intensity of the G band to 2D band (I_G/I_{2D}) can be used to indicate the thickness of GFs. The higher ratio indicates to the thicker graphene (Choe *et al.*, 2010). Shown in Fig 4, the intensity ratios decrease as the time of sonication increases.
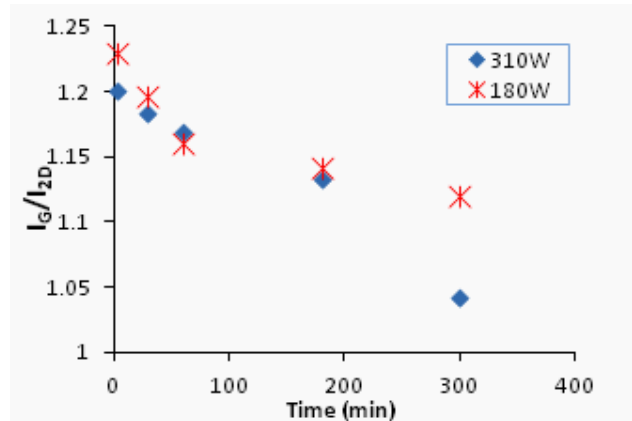
Fig. 4: Area ratios of G band and 2D band (I_G/I_{2D}) of 310W and 180W of ultrasonication power.

For 180W of sonication power, the ratio reducing from 1.23 to 1.12 from 3 minutes to 300 minutes, whereas with the sonication power of 310W, we can distinguish the ratio changing is reduced from 1.2 (3mins) to 1.04(300mins. From Fig.4, the values using 310W of sonication power have more significant difference compared to 180W. Based on these values we can conclude that the GFs produced with high power of sonication are thinner compared to low power. Even though that 2D band cannot identify the layers changing of GFs, but I_G/I_{2D} shows that the thickness of layers reduces.

Thermal Stability:

TGA was utilized to investigate the thermal stability of carbonerous materials. The disordered or amorphous carbon tended to be oxidized at around 500°C due to the lower activation energies for oxidation. However a well graphitized structure started to oxidize at higher temperature around 800°C (Teng *et al*., 2011). The GFs can be said to start the degradation temperature at 100°C related to the removal of physically adsorbed water (Gedler *et al*.,2012).

Fig.5 shows the analysis of selected GFs in nitrogen atmosphere. We can hardly identify the percentage degradation of GFs in Fig.5a due to the stability of GFs towards increasing of temperature. Hence, the Fig. 5b is the enlarged image from Fig. 5a for more detailed values. Fig. 5b shows that the GFs produced by this method were thermally stable, presenting maximum total weight loss of 11% at 1000°C (180W, 10 min about 2 μm in size). The rate of degradation of 180W, 300 and 310W, 300min happened faster between 200°C – 700°C compared to GNPs, but the rates were slowing down after 750°C made the total degradation was 8% at 1000°C for both types of GFs.

Initially GNPs show more stable compared to GFs between 200°C-600°C, but as the temperature increases, the percentage degradation of GNPs was increased by almost 12% in total. In the previous study [Wang *et al*.,2011,Teng *et al*., 2011], other graphitic form; graphene oxide (GO), was not performed a good thermal stability . The weight loss of GO occurred even below 100°C and the total weight loss was almost 40% at 800°C (Teng *et al*.,2011).
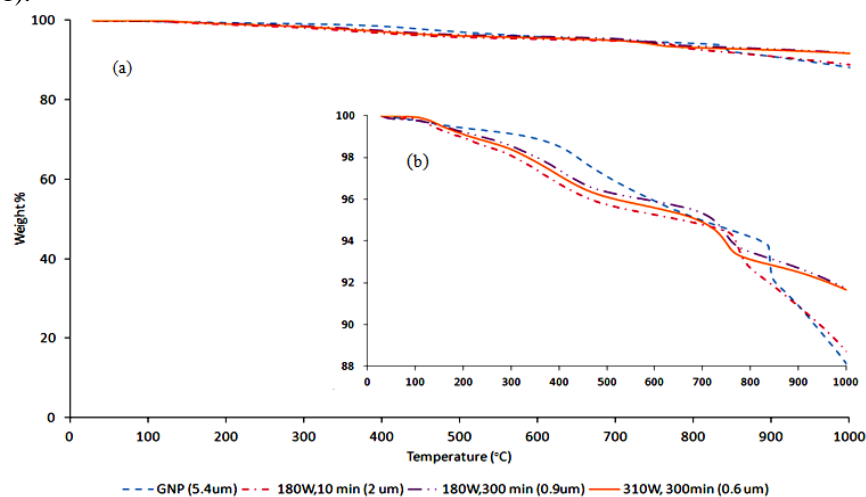

Fig. 5: TGA analysis of selected GFs under H_2 atmosphere.

This is maybe due to the large amount of oxygen-containing functional groups such as hydroxyls and carboxyls on the GO sheets (Shen *et al.*, 2009). By TGA analysis we proved that the GFs produced are thermally stable up to 1000°C.

Conclusion:

The results achieved can be summarized as follows:

1. Based on TEM images of GFs, it can be concluded that the size and the thickness of GFs were decreased when increasing the sonication time and power.

2. The area ratios of the G band to 2D band (I_G/I_{2D}) of Raman spectroscopy decreased indicating of decreased in thickness of GFs with the increasing of time and power of ultrasonication.

3. TGA thermograms of GFs showed that the GFs were stable with increasing of temperature in nitrogen atmosphere up to 1000°C(only less than 15wt% loss).

The GFs produced can be used further for other application such as polymer composites and lithium ion battery.

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